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NOLTR 70-258

WATER EXPOSURE OF STRESSED GRAPHITE FIBER COMPOSITES

By
M. L. Santelli
R. A. Simon

8 FEBRUARY 1971

NOL

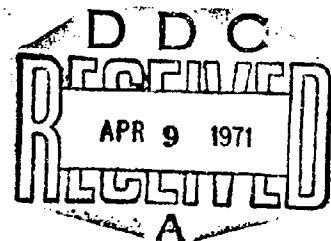## NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

ATTENTION

WATER EXPOSURE OF STRESSED
GRAPHITE FIBER COMPOSITES

Prepared by:
M. L. Santelli
R. A. Simon

ABSTRACT: Graphite fiber-epoxy resin composites were tested for their interlaminar shear and flexural strength retention under long-term loading at 50% of their ultimate strengths. Specimens were evaluated in both wet and dry environments. The largest deterioration occurred in the flexural specimens loaded in water. Under this condition, the per cent of strength retained varied from 0 to 81%, depending upon the resin system used.

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                      SILVER SPRING, MARYLAND

NOLTR 70-258   8 February 1971

WATER EXPOSURE OF STRESSED GRAPHITE FIBER COMPOSITES

This report describes the results of long-term loading tests on the
graphite fiber-reinforced plastic composites. The intent is to determine
the potential of such composites for use in Navy underwater structures.
With this in mind, particular attention was paid to the strength retention
properties in water. Earlier work in this area was reported in October
1968 (ref. (1)). This report covers the effort from July 1968 through
July 1970, funded by the Naval Ship Systems Command under task SHIP-
13576/SF51-544-102 Prob. 200.

The accuracy of the results reported is limited by occasional large
variations in the strength values obtained. However, the trends observed
are deemed sufficiently clear enough to permit making the materials
comparisons presented herein.

                            GEORGE G. BALL
                            Captain, USN
                            Commander

                            ALBERT LIGHTBODY
                            By direction

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REFERENCES

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INTRODUCTION

Much work has been done in recent years on the new high modulus, low density graphite fiber composites. These composites offer great potential for use in high performance struc' ~es where high strength-to-weight and modulus-to-weight ratios are : ortant. To design structures using these materials, it is obviously important to have a good understanding of their load carrying capabilities under various static and dynamic conditions.

Earlier work of this type ..as been reported in reference (⊥). Emphasis was on studying various carbonaceous fibers and composites with different fibers in the same resin matrix. This report describes studies on the long-term load carrying capability of graphite composites containing different resin systems but with a single fiber reinforcement. A distinct difference was found between the ability of graphite composites to withstand long-term static loading in air and their ability to withstand loading in water. While the lowest per cent shear strength retained after 22 weeks of stressed water exposure was 90%, the per cent flexural strength retained under this condition varied from 0 to 81% depending upon the matrix material. This compares with a minimum of 88% flexural strength retained for all dry conditions.

EXPERIMENTAL WORK

A. Approach

A review of the available graphite fibers, accompanied by a study of 12 epoxy resin systems, was made. From these results four graphite-epoxy composite systems were chosen. NOL ring composites were fabricated and cut up into short beam shear and flexural specimens. These specimens were then subjected to long-term shear and flexural loadings in both wet and dry environments. After exposures of 3 and 22 weeks, the specimens were removed from the fixtures and tested for strength retention.

B. Selection of Materials

1. Resin Systems. Twelve epoxy resin systems were tested for various physical and mechanical properties before and after water boil. Table 1 gives a listing of the resin systems selected for these tests.

2. Composite Systems. Modmor II-S fiber was selected as one of the best available graphite fibers and was used in fabricating all of the composite systems. The resins used as matrix materials for the four composites were Systems 5, 6, 7, and 9, as listed in Table 1. These were chosen for their strength and strength retention properties. System 9 is the same resin as was used in the previous long term loading tests (ref. (1)).

C. Fabrication of Specimens

1. **Resin Specimens.** The resin specimens used were standard tensile specimens, ASTM D638-67T, Type I. These were cut from 1/8" thick plates of cast epoxy.

2. **Composite Specimens.** NOL rings were wound in accordance with ASTM 2291-67 using Modmor II-S fiber. Resin systems 6, 7 and 9 were wet wound in a vacuum. System 5, because of its high viscosity, was prepregged and then wound onto a heated ring mold. The cured rings were machined and cut into flexural specimens and short beam shear specimens.

D. Testing Procedure

1. **Resin Systems.** The twelve epoxy resin systems listed in Table 1 were tested for yield and ultimate tensile strengths, moduli, energy to break, and hardness. These properties were retested after a 72-hour water boil and the per cent weight gain measured. Some of the earlier systems tested (2, 5, 9 and 11) were water boiled only 6 hours.

2. **Composite Systems.** The fiber contents of the composite specimens were determined by heating samples at 600°C in a nitrogen atmosphere for 16 hours. Samples of the fiber and of each type of resin were run at the same time. For each system, the percent weight lost by the fiber, the resin, and the composite was measured, and these values were used to calculate the weight percent of fiber in the composite.

Groups of specimens from each system were tested to determine the average shear and flexural strengths of the composites. All shear tests in this program were short-beam shear (ASTM D2344-67), made at a span-to-depth ratio of 5. All flexural tests were in four-point bending with a span of 5.08 cm (2.00 inches) between the lower supports and a span of 1.27 cm (0.50 inches) between the upper loading rods. Ratios of lower span to specimen thickness varied from 15.7 to 16.8.

The remaining specimens from each system were divided into two equal groups. The first group was left unloaded. The second was loaded in fixtures and stressed to 50% of the ultimate strength for the system. The stress on each individual specimen was based on its original measured width and thickness. After 24 hours, the specimens were reloaded, that is, the load on each specimen was brought back up from the load to which it had crept after 24 hours to the original load. The groups of specimens were then further divided. Half of the loaded specimens and half of the unloaded specimens were placed in shallow water (deionized tap water) at 70 ±2°F. The rest were left in air at 50 ±5% R.H., 70 ±2°F. A breakdown of the test environments for the specimens in each system is given in Figure 1.

Figure 2 shows a top view of a flexural fixture as it is being assembled. Shear fixtures are shown in Figure 3. The loading of flexural and shear fixtures, using an Instron test machine, is pictured in Figures 4 and 5, respectively.

After three weeks, some of the specimens were unloaded and tested for strength retention. The loads on the remaining specimens

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were restored at this time to their original values. To maintain a relatively constant stress level, the load on each of these specimens was checked at three-week intervals throughout the test. If necessary, the specimen was reloaded. Actually, after six weeks there was very little creep evident.

After 22 weeks, the remaining specimens were removed from their test environments and tested for strength retention.

The above procedure is essentially the same as that used for the "long-term water exposure" tests of ref. (1). The main difference is that in the earlier tests the specimens were not reloaded at any time after the initial load was applied.

RESULTS AND DISCUSSION

A. Resin Study

The results of the tests run on the twelve resin systems are summarized in Table 2. The "as cast" tensile yield strengths ranged from $27.6 \times 10^6 n/m^2$ (4000 psi) for System 2 to $62.1 \times 10^6 n/m^2$ (9000 psi) for System 5. System 6 had the highest ultimate strength, $125 \times 10^6 n/m^2$ (18,150 psi), and the highest initial modulus, $5.1 \times 10^9 n/m^2$ (0.75×10^6 psi). The lowest ultimate strength, $50.1 \times 10^6 n/m^2$ (7270 psi), and the lowest modulus, $2.0 \times 10^9 n/m^2$ (0.30×10^6 psi), were those of System 12. The 72 hour water boil resulted in weight gains of 1 to 3% for most resin systems. System 6 was an exception with an unusually high weight gain of 9.7%. Yield strength retention after the water boil varied considerably with some values higher than the original strengths and others approximately 40% lower. Ultimate tensile strength retention ranged from 64% to 86% for the systems subjected to 72 hour water boil. System 7 exhibited the best overall strength retention properties with 92% yield strength retention and 86% ultimate strength retention after 72 hour water boil.

B. Composite Study

The composite fiber contents and average initial strengths determined from the preliminary tests on the composite control specimens are listed in Table 3. Void contents calculated using the manufacturer's value of fiber density, measured resin and composite densities (see Tables 1 and 3), and the volume fractions of fiber listed in Table 3 ranged from -0.3% to -1.4%. These negative values indicate that some or all of the values which are used in calculating the void contents are not known with sufficient accuracy. While the resin and composite densities can be measured to within a fraction of a percent, the fiber density given by the manufacturer and the weight fraction of fiber determined by our pyrolysis method (see "Experimental work", Section D) are probably only accurate to within ±2 percent. A 2% increase in the value of fiber density, for example, would change the calculated void content of the System 5 composites from -0.3% to +0.9%. Because of the inaccuracies in the procedure, specific values of void content for each sample are not presented in this report. But from the calculations and from past experience with vacuum winding, the composite void contents are

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generally from 0-2%.

The results of the long-term environmental test in terms of percent
strength retained are given in Figures 6 and 7. Figure 8 shows the percent
weight gained by the composite shear specimens. The percent weight gained
by the flexural specimens was very similar. None of the systems tested
averaged less than 86% shear strength retention for any test condition.
Shear strength retention is thus considered good especially when the average
values are examined together with the variations involved. Average
retention for shear specimens stressed in water ranged from 90 to 101%.
Flexural strength retention, on the other hand, varied from 0 to 81% for
specimens loaded underwater. This is particularly significant since the
lowest value of flexural strength retention for all dry conditions was
88%. As found by others (refs. (1)), (2) and (3)), there is also no excessive
loss of flexural strength simply from unstressed exposure to water. In our
test a maximum of 9% flexural strength was lost by "wet-unloaded" specimens.
The previous report (ref. (1)) noted that "RAE (graphite) composites
survived both shear and flexural tests fairly well" except for "flexural
specimens in a wet environment under load."

Weight gain data (Fig. 11) show a tendency of loaded wet specimens
to absorb 0.1 to 0.2% more water than unloaded wet ones in a 22 week period.
This correlated nicely with strength deterioration results. Water pickup
alone, however, does not seem to be a good indication of the ability of
composites to withstand long-term loading in water. All of the "wet-loaded"
flexural specimens in System 9, for example, failed in the fixture before
the 22 weeks was up, while those in Systems 6 and 7 showed about 80% strength
retention. Weight gained by System 6 specimens, however, was the highest
at 2.0% while Systems 7 and 9 both gained 0.7%.

The composites fabricated using the ERLA 4617 and the ERX-16 resins
(both relatively new) withstood stressed water exposure better than the
composites made with the other resins. Still, even the 4617 and ERX-16
systems showed 20% loss of the flex strength in the loaded-wet condition.
It would appear, therefore, that water immersion under flexural stress
is a good indication of the ability of graphite composites to withstand
water environments. This was also found to be the case previously (ref. (1)).
Studies similar to ours were done simultaneously at the Fiberite Corporation
(ref. (4)). Results are not entirely comparable, probably because the test
conditions were somewhat different. However, Fiberite also selected resin
systems on the basis of long-term water exposure of graphite composites under
flexural load. From a theoretical point of view, the question remains as to
what type of deterioration took place in our test to cause flexurally
stressed specimens to weaken and not those stressed in shear. This
deterioration of specimens flexurally loaded in a water environment does
not preclude the use of graphite composites for underwater structures.
This test is particularly severe, and is a materials test to show differences
in materials under extreme conditions. A real structure, with no exposed
cut ends and under a compressive stress which tends to close cracks and voids,
would survive much better underwater than these test specimens. This has
been shown to be true on structures made from glass reinforced plastics.
Alfers and Graner (ref. (5)) found that glass reinforced polyester laminates
taken from the fairwater of a submarine retained 88% flexural strength
after 5 years of service. Cylinders made at NOL from S-glass and an Epon

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828 resin system showed almost no deterioration after being exposed for over 3 years to external water pressures that were 70% of the breaking pressure for control cylinders. This good strength retention of the cylinders occurred even though samples of this composite showed a 25% loss of short beam shear strength after only 6 hours of water boil (ref. (6)). Using the best materials from this work with graphite composites, the construction and testing of model or typical structures would show the stability of these materials in their intended applications.

SUMMARY AND CONCLUSIONS

There is a distinct difference between the ability of graphite composites to withstand long-term static loading in air and their ability to withstand similar loading in water. None of the composites tested showed a significant loss of strength when loaded dry. In water, however, two of the systems failed completely under long-term flexural loading. The other two lost about 20% of their original flex strength in 22 weeks of wet loading. Thus, it appears that graphite composites are subject to deterioration when loaded in water. The deterioration may be limited or quite extensive depending upon the resin system used. Water exposure alone, without loading, does not result in any significant strength loss. Nor does shear loading in water show any deterioration in a 22 week period. Water immersion under flexural stress is the only combination found in this series of tests to indicate serious deterioration in the composites.

RECOMMENDATIONS AND FUTURE PLANS

Further testing of graphite composites in water environments is needed. For example, although the ERLA 4617 resin did quite well in this test, ERLB 4617 has been reported to be superior for use in water and should be evaluated. Underwater testing of actual structural models would give useful information. Future work at NOL will be directed toward fabrication and testing of filament would cylinders.

ACKNOWLEDGMENTS

TABLE 1

RESIN SYSTEMS

System No.	Components	Parts by Wt.	Cure Cycle	Density of Cast Re (g/cc)
1	Epon 826 Methylene Dianiline	100 28	2 hrs at 80°C 16 hrs at 130°C 2 hrs at 160°C	1.197
2	Epon 826 Nadic Methyl Anhydride Benzyldimethylamine	100 85 3.5	4 hrs at 90°C 16 hrs at 150°C 2 hrs at 200°C	1.218
3	Epon 826 Ethyl Methyl Imidazole	100 15	4 hrs at 75°C 16 hrs at 150°C	1.182
4	Epon 826 Ethyl Methyl Imidazole Nadic Methyl Anhydride	100 3.5 85	4 hrs at 90°C 16 hrs at 150°C 2 hrs at 200°C	1.220
5	Den 438 Nadic Methyl Anhydride Benzyldimethylamine	100 85 1.5	4 Hrs at 90°C 16 hrs at 150°C 2 hrs at 200°C	1.250
6	ERLA 4617 Meta-Phenylene Diamine	100 27	4 hrs at 85°C 3 hrs at 120°C 16 hrs at 160°C	1.273
7	ERX-16 Curing Agent Y	100 44	16 hrs at 66°C 4 hrs at 93°C 4 hrs at 135°C 8 hrs at 177°C	1.218
8	ERE-1359 Nadic Methyl Anhydride Benzyldimethylamine	100 116 2	4 hrs at 90°C 16 hrs at 150°C 2 hrs at 200°C	1.272
9	ERL 2256 ZZL 0820	100 27	3 hrs at 100°C 3 hrs at 150°C	1.230
10	Epon 826 Epon 1031 Nadic Methyl Anhydride Benzyldimethylamine	100 100 180 1.1	2 hrs at 100°C 6 hrs at 150°C	1.248
11	Epon 828 Curing Agent D CTBN (Hycar liquid rubber)	100 12 5	1 hr at 63°C 1 hr at 150°C	1.161

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TABLE 1
(Continued)

System No.	Components	Parts by Wt.	Cure Cycle	Density of Cast Resin (g/cc)
12	Epon 828	100	2 hrs at 71°C	1.092
	Dodecenyl Succinic Anhydride	115.9	4 hrs at 150°C	
	Empol 1040	20		
	Benzyldimethylamine	1		

TABLE 2

AVERAGE PROPERTIES OF RESIN SPECIMENS BEFORE AND AFTER WATER BOIL

| System	Preparation	Number of Specimens	Percent Weight Gain	Yield Strength (n/m² x 10⁻⁶)	Ultimate Strength (n/m² x 10⁻⁶)	Initial Modulus (n/m² x 10⁻⁹)	Energy to Break (joules)	Rockwell M Hardness	
								Rockwell Reading	Ball Indentation (mm)
1	As Cast	4	-	29.6	71.5	2.4	6.4	107	0.46
	72 Hr. Boil	5	1.87	33.1	53.0	1.9	2.6	103	0.56
2	As Cast	4	-	27.6	65.0	2.5	-	104	0.53
	6 Hr. Boil	3	0.50	34.5	54.1	2.5	1.4	104	0.56
3	As Cast	4	-	42.1	82.4	3.1	9.4	102	0.56
	72 Hr. Boil	5	3.36	35.2	53.6	2.4	1.8	86	0.89
4	As Cast	4	-	44.8	74.9	3.2	2.9	112	0.36
	72 Hr. Boil	5	1.35	54.7	54.7	2.7	1.1	113	0.36
5	As Cast	6	-	62.1	69.8	2.8	1.4	118	0.25
	6 Hr Boil	6	0.55	44.1	66.7	2.8	1.8	119	0.23
6	As Cast	4	-	55.2	125	5.1	6.0	124	0.13
	72 Hr. Boil	4	9.70	35.9	85.9	5.1	4.1	105	0.51
7	As Cast	4	-	48.5	61.7	4.2	1.1	124	0.13
	72 Hr Boil	4	2.16	44.6	52.8	4.1	0.8	118	0.25
8	As Cast	4	-	-	-	3.1	-	110	0.41
	72 Hr Boil	3	1.63	60.6	60.6	3.1	1.4	110	0.41
9	As Cast	6	-	55.2	98.7	2.9	6.9	118	0.25
	6 Hr Boil	6	1.00	45.5	85.8	2.9	5.5	115	0.30
10	As Cast	3	-	-	-	3.1	2.1	121	0.18
	72 Hr Boil	4	2.17	52.0	52.0	2.8	1.0	119	0.23

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TABLE 2 (continued)

System	Preparation	Number of Specimens	Percent Weight Gain	Yield Strength (n/m² x 10⁻⁶)	Ultimate Strength (n/m² x 10⁻⁶)	Initial Modulus (n/m² x 10⁻⁹)	Energy to Break (Joules)	Rockwell M Hardness Rockwell Reading	Ball Indentation (mm)
11	As Cast	6	-	35.9	61.5	2.5	4.0	80	1.0
	6 Hr. Boil	7	1.15	33.1	52.5	1.8	8.1	69	1.2
12	As Cast	6	-	31.7	50.1	2.0	3.2	-	-
	72 Hr. Boil	6	-	18.6	32.0	1.6	6.2	-	-

TABLE 3

PROPERTIES OF COMPOSITE CONTROL SPECIMENS

System	Density	Weight Percent of Fiber	Volume Percent of Fiber	Average Shear Strength (n/m² x 10⁻⁸)	Coefficient of Variation (Shear)	Average Flexural Strength (n/m² x 10⁻⁸)	Coefficient of Variation (Flexural)
5	1.55	68	60	0.814	0.022	14.3	0.051
6	1.48	46	41	1.067	0.030	11.6	0.120
7	1.46	55	46	1.025	0.053	13.4	0.050
9	1.52	60	53	0.898	0.040	14.2	0.049

NOTE: Experience has shown void contents for composites wound in a vacuum to be in the range 0 to 2%.
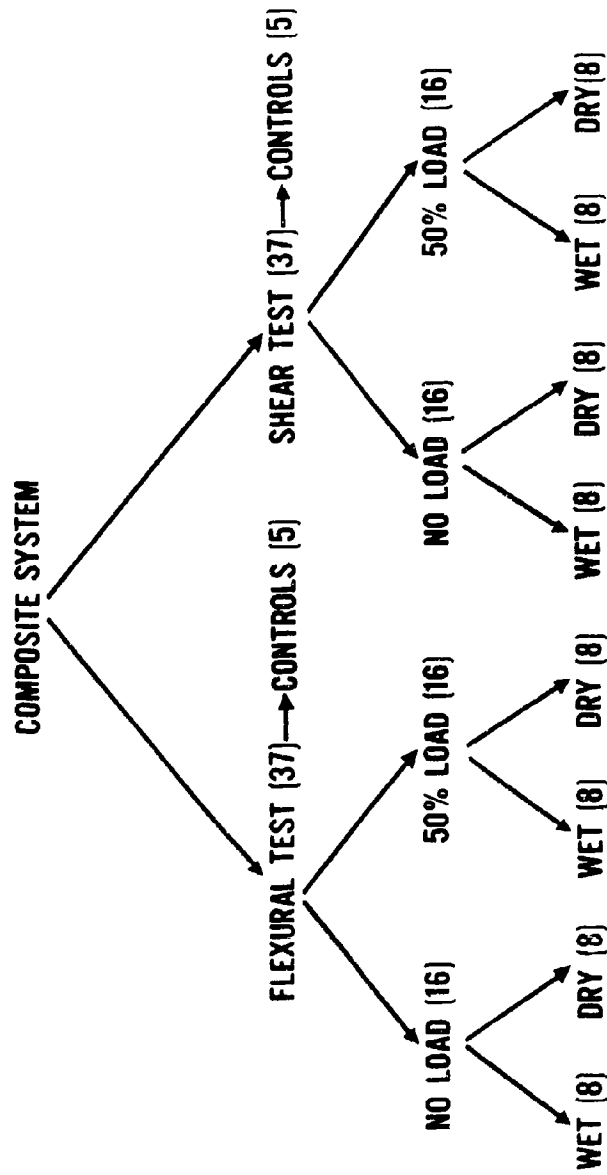
FIG. 1 ENVIRONMENTS FOR COMPOSITE SPECIMENS
IN STATIC LOADING TEST

NUMBERS IN BRACKETS INDICATE NUMBER OF SPECIMENS
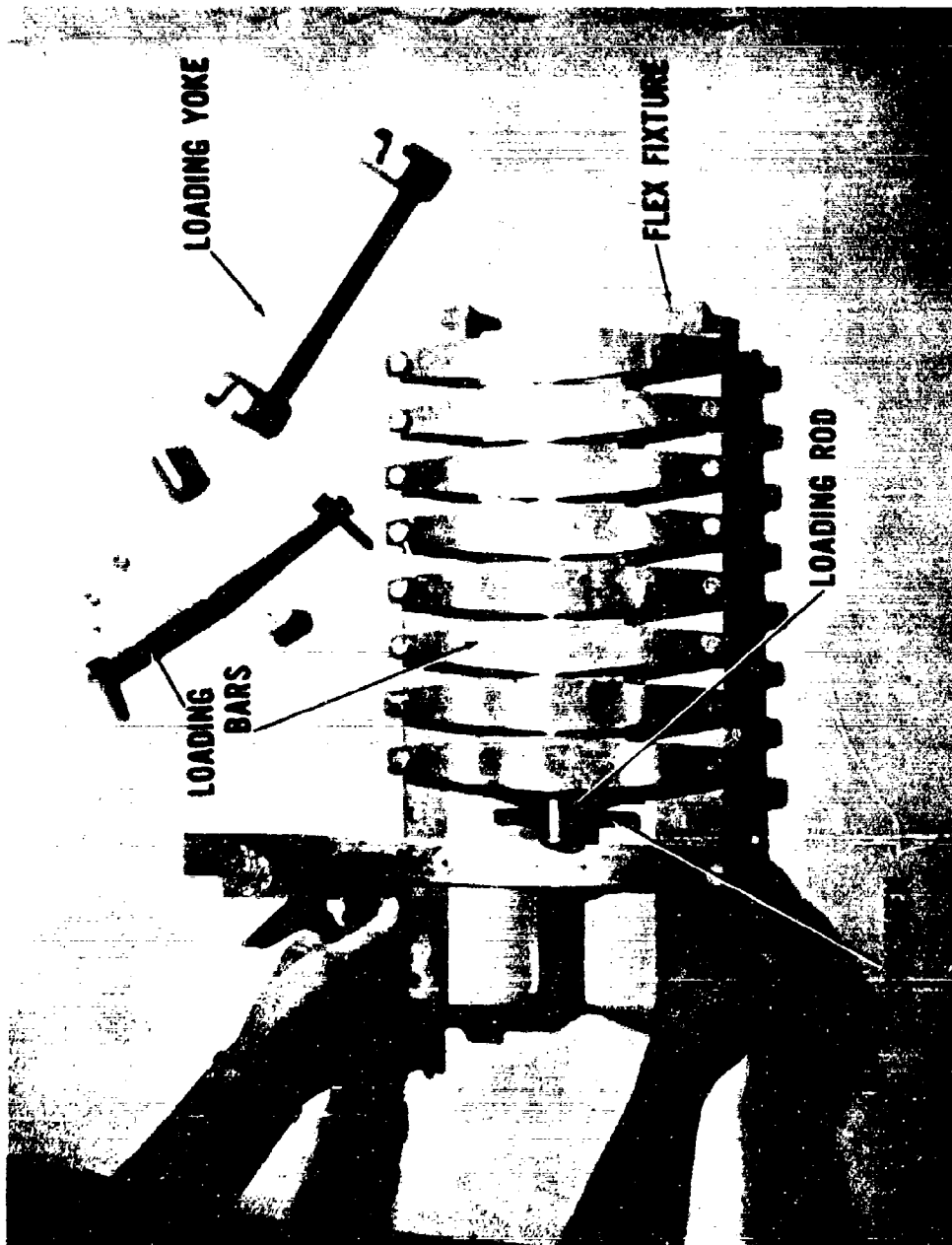
FIG. 2 ASSEMBLY OF STATIC FLEXURAL LOADING FIXTURE
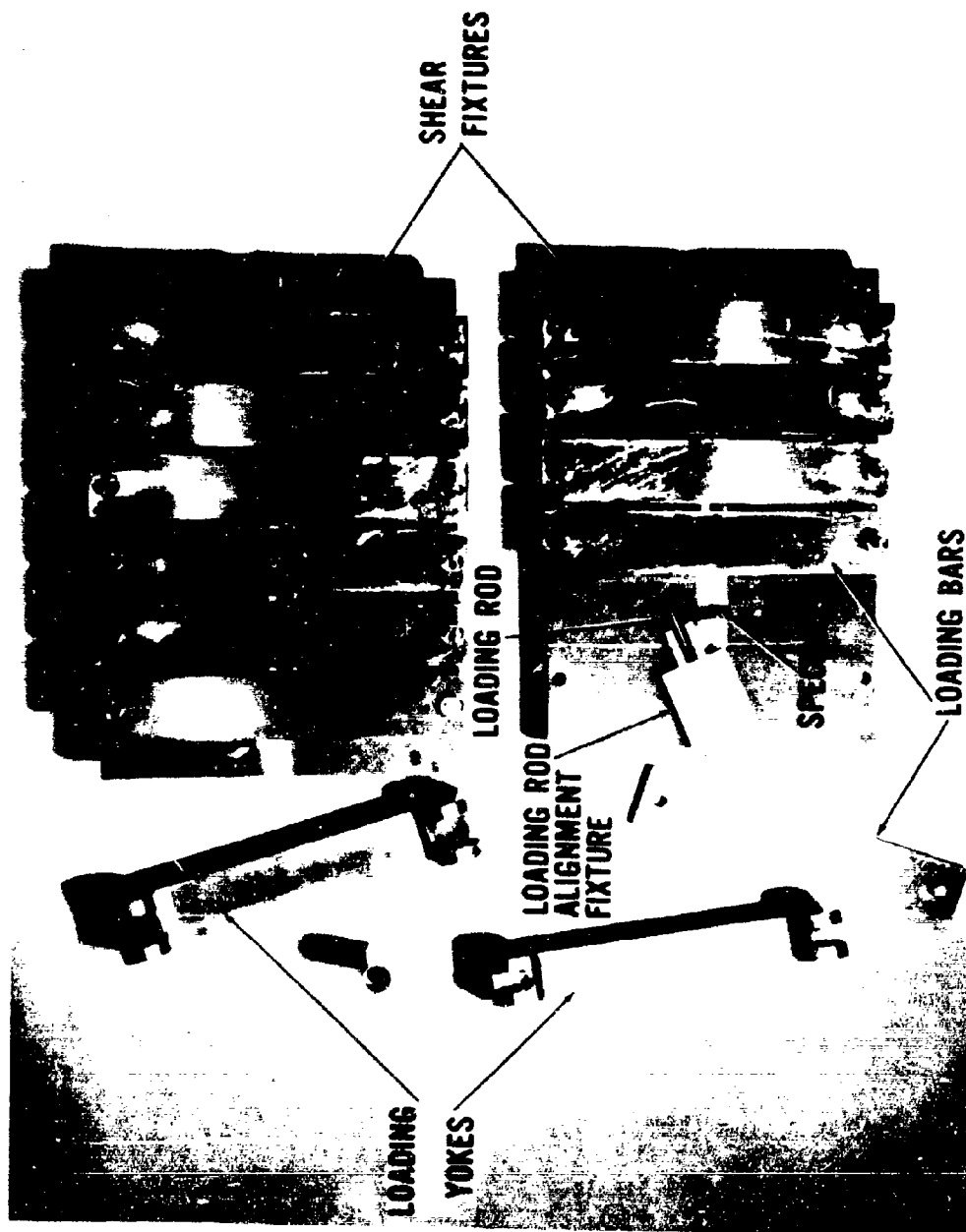
FIG. 3 TOP VIEW OF STATIC SHEAR LOADING FIXTURES
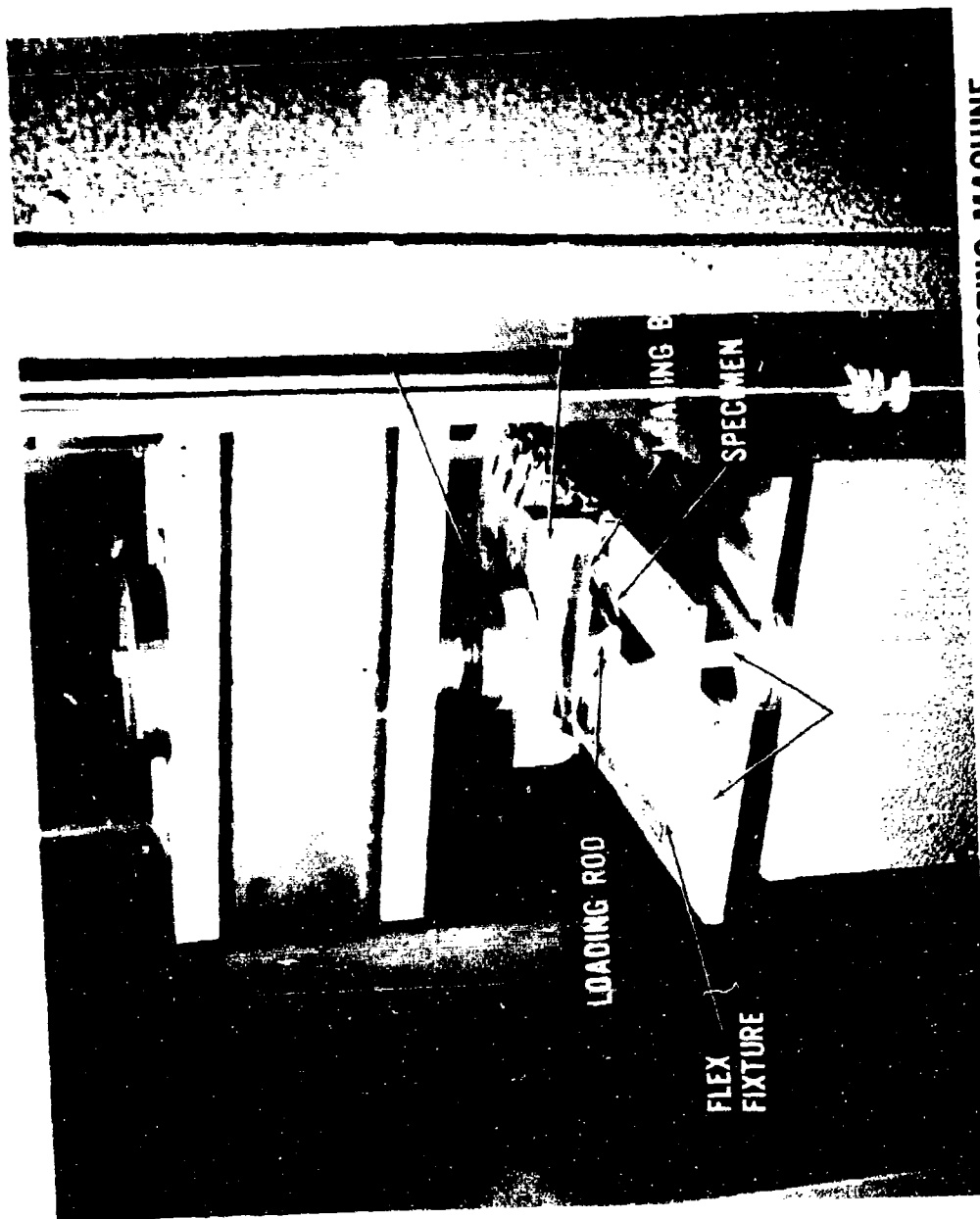
FIG. 4 LOADING OF FLEX FIXTURE IN INSTRON TESTING MACHINE
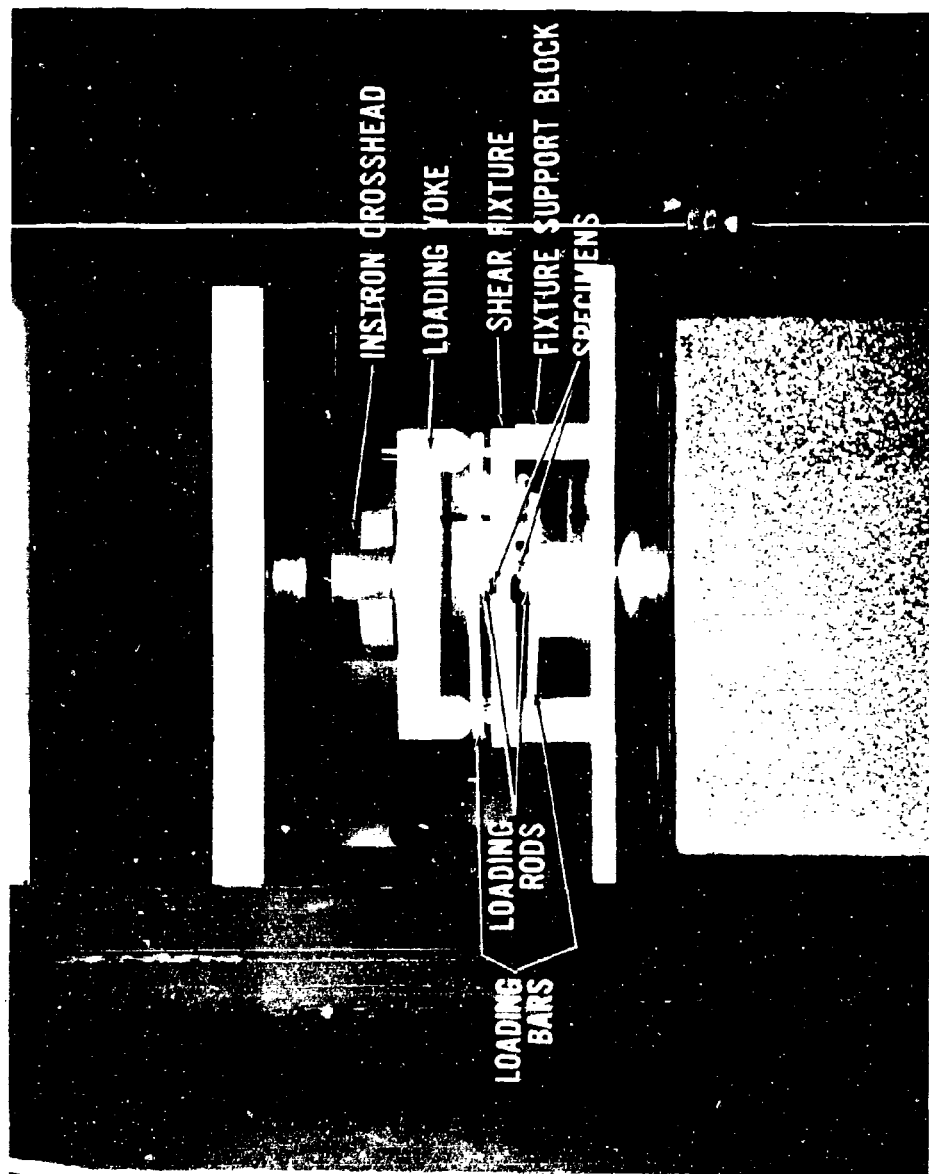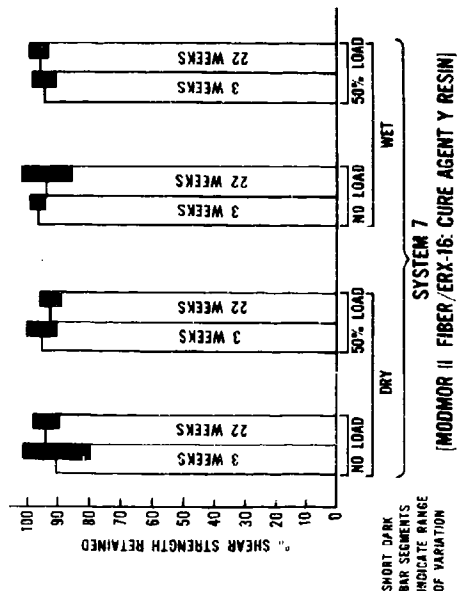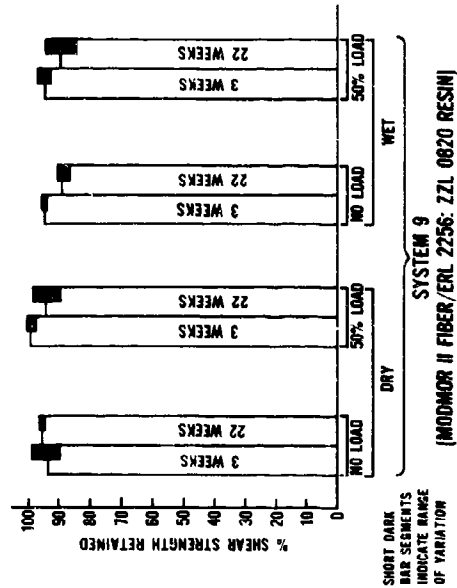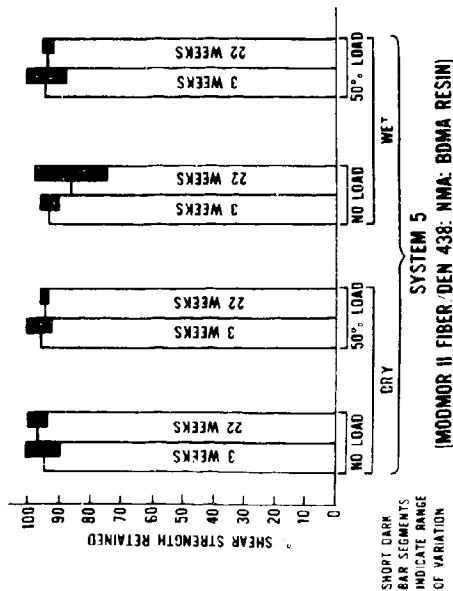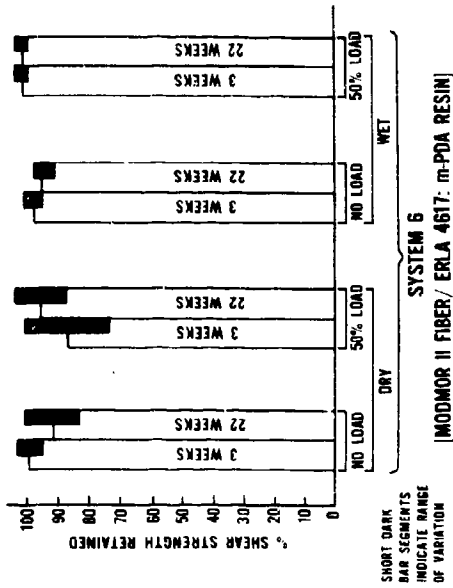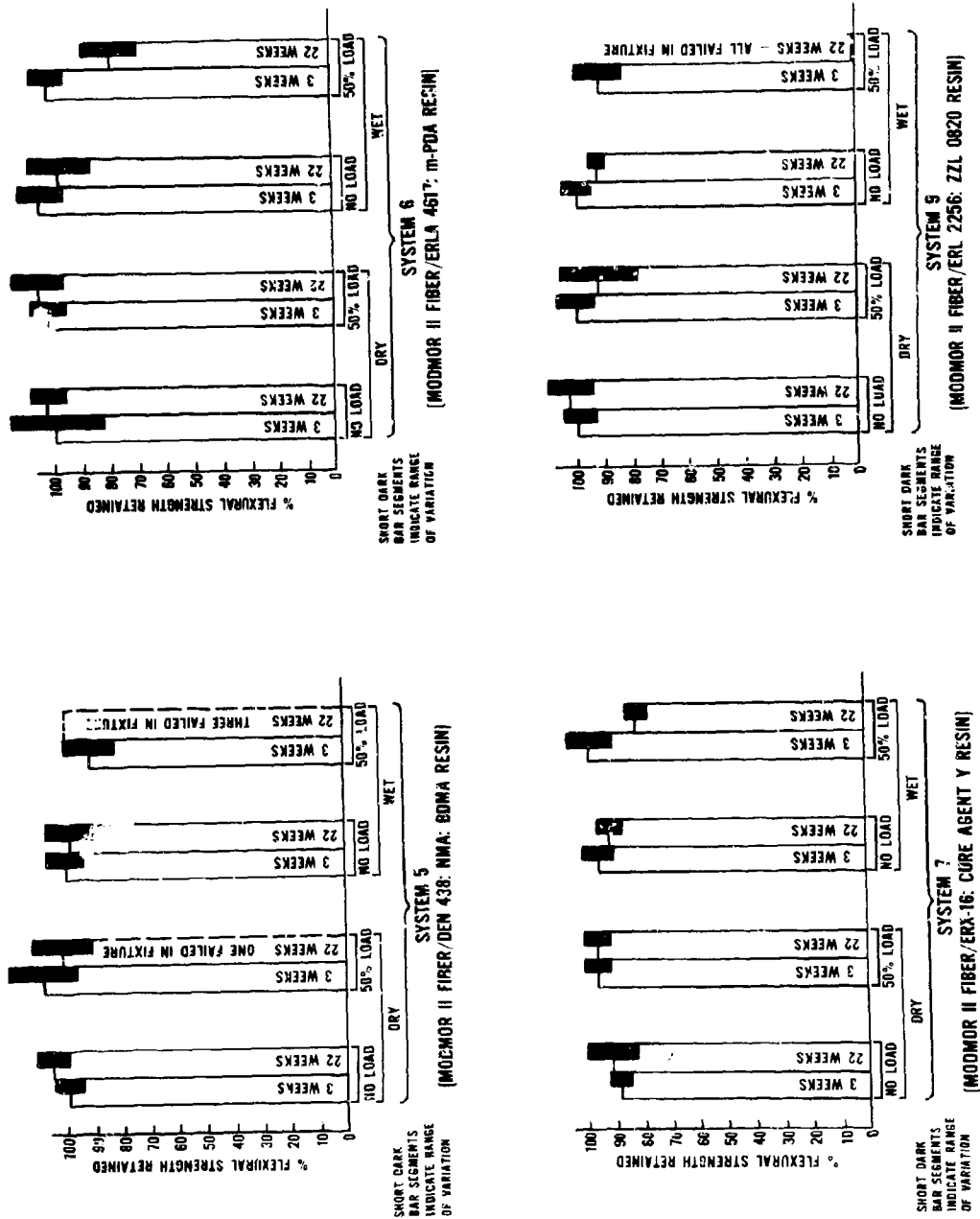
FIG. 5 LOADING OF SHEAR FIXTURE IN INSTRON TESTING MACHINE

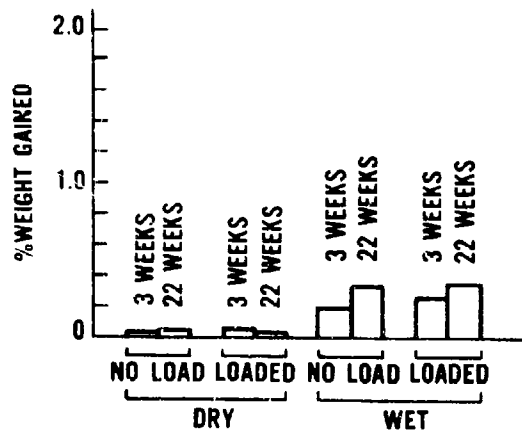FIG. 6 COMPOSITE STRENGTH RETENTION IN STATIC SHEAR LOADING
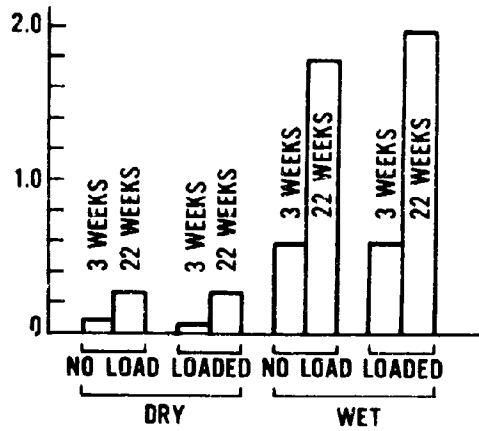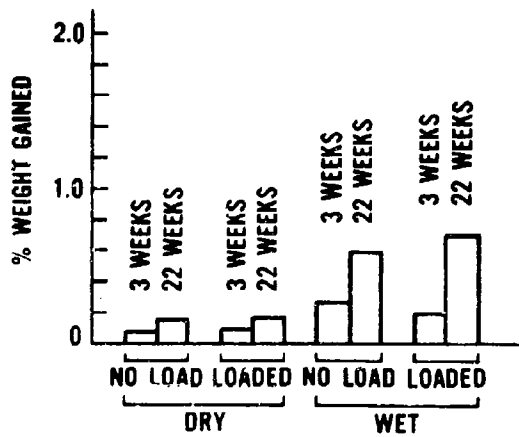
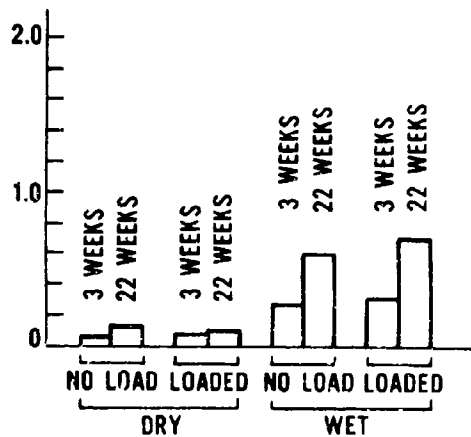FIG. 7 COMPOSITE STRENGTH RETENTION IN STATIC FLEXURAL LOADING

SYSTEM 5
(MODMOR II FIBER/DEN
438:NMA:BDMA RESIN)

SYSTEM 6
(MODMOR II FIBER/ERLA
4617:m-PDA RESIN)

SYSTEM 7
(MODMOR II FIBER/ERX-16:
CURE AGENT Y RESIN)

SYSTEM 9
(MODMOR II FIBER/ERL2256:
ZZL0820 RESIN)

FIG. 8 PERCENT WEIGHT GAIN OF COMPOSITE SHEAR SPECIMENS

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Naval Ordnance Laboratory Silver Spring, Maryland 20910	Unclassified
	2b. GROUP

3. REPORT TITLE

WATER EXPOSURE OF STRESSED GRAPHITE FIBER COMPOSITES

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Annual

5. AUTHOR(S) *(First name, middle initial, last name)*

M. L. Santelli
R. A. Simon

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
8 February 1971	23	6

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. Task SHIP-13576/SF51-544-102, Problem 200	NOLTR 70-258
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Naval Ship Engineering Center Prince Georges Center Hyattsville, Maryland 20782

13. ABSTRACT

Graphite fiber-epoxy resin composites were tested for their interlaminar shear and flexural strength retention under long-term loading at 50% of their ultimate strengths. Specimens were evaluated in both wet and dry environments. The largest deterioration occurred in the flexural specimens loaded in water. Under this condition, the per cent of strength retained varied from 0 to 81%, depending upon the resin system used.

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Graphite Fiber Composites Reinforced Plastics Water Exposure High Modulus Structural Material						